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**Addition Products Obtained from the Chlorination
of 1,2-Dichloronaphthalene**

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Chlorination of naphthalene gives besides products of substitution appreciable amounts of naphthalene tetrachlorides (1,2,3,4-tetrachloro-1,2,3,4-tetrahydronaphthalenes), which usually exist in several forms. The stereochemistry of these addition products, four of the six possible tetrachlorides, has recently been established by de la Mare and his co-workers by the kinetic study and proton magnetic resonance spectroscopy (Table I).¹⁾ They have observed the remarkable dependence of the structures of addition products on the reaction conditions: in the dark and without catalyst, the main adduct was the α -tetrachloride, accompanied by some δ -isomer: added electrolytes, however, changed the proportion greatly in favor of the latter isomeride. Under the homolytic conditions involving irradiation or catalysis of peroxides, the addition products were the γ - and ϵ -tetrachlorides in the approximate ratio 2 : 3.

With an intent to know if the local accumulation of chlorine atoms on the naphthalene nucleus may have any effect on the geometrical configurations of tetrachlorides formed, 1,2-dichloronaphthalene was chlorinated under a similar condition as that used for 1,5-dichloronaphthalene,²⁾ which was found to give a tetrachloride with the α/δ -configuration. Chlorine take-up occurred slowly, and after two days yellow color of chlorine almost disappeared. The solvent was removed under reduced pressure and the residual syrup was chromatographed on silica gel with light petroleum (bp 40–60°C) as eluent. A mixture of polychloronaphthalenes eluted first, then a syrupy product followed. After stood for several days, addition products separated out from the syrupy fractions. These adducts consisted of two different tetrachlorides: the most easily isolated was 1,2,3,4,5,6-hexachloro-1,2,3,4-tetrahydronaphthalene melting at 73–74°C, which constituted the major part of the early eluates. From the late eluates another tetrachloride melting at 103–104°C was obtained. Formation of any stable dichlorides could not be observed.

In contrast to the general findings that the most readily formed addition product has the α -configuration under ionic conditions and the γ -configuration under homolytic conditions, the main addition product melting at 73–74°C was found to possess neither one of these configurations as would be realized from the NMR signals summarized

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in Table II. The magnitude of coupling constants revealed the presence of one axial-pseudoaxial pair ($J=8.8$ Hz), one axial-equatorial pair ($J=2.9$ Hz), and one equatorial-pseudoaxial or equatorial-pseudoequatorial pair ($J=2.7$ Hz) of protons in the alicyclic system. Two doublets at 2.20 and 2.01 τ with the high coupling constant ($J=8.8$ Hz) are due to *ortho* aromatic protons. The strongly deshielded aliphatic proton at 4.03 τ should be located at the 4-position near to the 5-chlorine atom. Thus, the tetrachloride would probably have the structure of either I or II, that is, ϵ -configuration or still unknown β -configuration. A stereochemical relation of H₃ and H₄ atoms can not be determined definitely by the NMR data alone, since the low coupling constant ($J=2.7$ Hz) could be attributed either to a *cis* (equatorial-pseudoaxial) or a *trans* (equatorial-pseudo-equatorial) configuration.

The high-melting isomer, a minor component of the adduct fraction, was found to have the α -configuration by the analysis of the NMR data summarized in Table II. The

Table I. Conformations of Naphthalene Tetrachlorides in Solution.

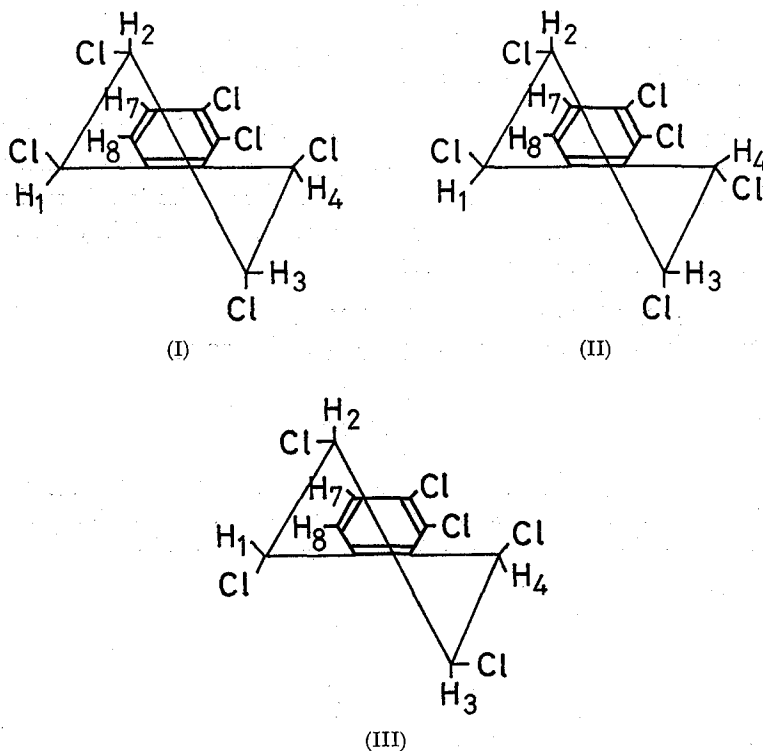
Compound	Mp (°C)	Solvent	Chlorine positions
α -Tetrachloride	182	Acetone	1 <i>a'</i> . 2 <i>e</i> . 3 <i>e</i> . 4 <i>a'</i>
γ -Tetrachloride	134	Chloroform	1 <i>e'</i> . 2 <i>e</i> . 3 <i>e</i> . 4 <i>e'</i>
δ -Tetrachloride	96	Chloroform	1 <i>a'</i> . 2 <i>e</i> . 3 <i>e</i> . 4 <i>e'</i>
ϵ -Tetrachloride	85 - 87	Chloroform	1 <i>a'</i> . 2 <i>a</i> . 3 <i>e</i> . 4 <i>e'</i> \rightleftharpoons 1 <i>e'</i> . 2 <i>e</i> . 3 <i>a</i> . 4 <i>a'</i>

Table II. ¹H NMR and IR Spectra of 1,2,3,4,5,6-Hexachloro-1,2,3,4-Tetrahydronaphthalenes

Compound	Low-melting tetrachloride	High-melting tetrachloride
MP (°C)	73 - 74	103 - 104
τ (p.p.m.)		
Aromatic		
7-H	2.01	2.24
8-H	2.20	2.56
Aliphatic		
1-H	4.30	4.56
2-H	5.46	5.57
3-H	4.88	4.82
4-H	4.03	4.30
Coupling constants (Hz)		
$J_{1,2}$	8.8	3.3
$J_{2,3}$	2.9	10.3
$J_{3,4}$	2.8	4.4
$J_{7,8}$	8.8	8.6
IR (cm ⁻¹)	1402, 1304, 1240, 1161, 1143, 930, 835, 814, 800, 770, 698	1397, 1265, 1198, 1171, 976, 951, 854, 839, 821, 760, 720, 709, 653

alicyclic system has two pairs of axial-pseudoequatorial protons ($J=3.3$ and 4.4 Hz) and one pair of axial-axial protons ($J=10.3$ Hz), consistent with the α -configuration of the product. Two doublets at low field region (2.56 and 2.24τ) are due to the *ortho* hydrogen atoms of aromatic ring, as is apparent from their high coupling constant ($J=8.6$ Hz). The α -hydrogen atom with signals in the low field (4.30τ) should be at the 4-position near to the chlorine atom. By analogy with the well-established α -naphthalene tetrachloride, the stereochemistry may be formulated as III.

The stereochemistry of the low-melting adduct as well as the mode how such a tetrachloride with the less common configuration can be derived from 1,2-dichloronaphthalene will be subject to further study.



EXPERIMENTAL

Melting points were determined with a hot stage and are uncorrected. IR spectra were recorded on Nujol mulls with a Unicam SP 200 infrared spectrophotometer. ^1H NMR spectra were obtained in deuteriochloroform with a Perkin-Elmer 60 M Hz spectrometer against internal TMS.

Chlorination of 1,2-Dichloronaphthalene: To a solution of chlorine (6.3 g) in cold chloroform (150 ml), 1,2-dichloronaphthalene (10.0 g) was added all at once. The flask was loosely stoppered and kept in a dark place for two days. Then the solvent was removed under reduced pressure and a pale yellow syrup (*ca.* 13.2 g) was left in a refrigerator fortnight. The oil became turbid but no crystalline precipitate was obtained. Chromatographic treatment of this oil on silica gel using light petroleum (bp 40 – 60°C)

as eluent gave four fractions in the order of elution: a mixture of polychloronaphthalenes, a mixture of both substitution and addition products, a pale yellow syrupy substance mainly composed of the low-melting tetrachloride, and a sticky syrup containing the high-melting isomeric tetrachloride. The first fraction (3.44 g) gave on standing some amounts of white crystals, readily soluble in cold light petroleum, which were found to be a complicated mixture of polychloronaphthalenes. The second fraction (2.42 g) on fractional crystallization from ligroin gave a tetrachloride (0.36 g) as prisms melting at 72–74°C. The third fraction (4.21 g) almost solidified to a soft crystalline mass, which was recrystallized from hot ligroin (bp 80–100°C) to give the same tetrachloride as large prisms (2.36 g), mp 73–74°C. Infrared spectral inspection revealed that the non-crystallizable part was also composed mostly of this tetrachloride.

Found: C, 35.56; H, 1.67; Cl, 62.61%.

$C_{10}H_6Cl_6$ requires C, 35.44; H, 1.79; Cl, 62.77%.

The last fraction (1.02 g) was a sticky light brown syrup, from which on prolonged standing white crystals separated. Removal of the syrupy part with hot light petroleum (bp 60–80°C) gave another tetrachloride (0.5 g), which on recrystallization from ligroin gave plates melting at 103–104°C. Seeding gave a better result. Slightly soluble in cold ligroin and readily soluble in hot benzene.

Found: C, 35.67; H, 1.31; Cl, 63.00%.

$C_{10}H_6Cl_6$ requires C, 35.44; H, 1.79; Cl, 62.77%.

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